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(21) 出願番号	特願平7-240590	(71) 出願人	000002934 武田薬品工業株式会社 大阪府大阪市中央区道修町四丁目1番1号
(22) 出願日	平成7年(1995)8月24日	(72) 発明者	安達 清 兵庫県神戸市灘区筑岡通1丁目2番3号
		(72) 発明者	梶崎 武雄 大阪府大阪市淀川区加島1丁目2-3-403
		(74) 代理人	弁理士 谷 良隆

(54) 【発明の名称】 電気二重層コンデンサの電極用活性炭

(57) 【要約】

【課題】これまで提案されてきた活性炭を分極性電極とする電気二重層コンデンサは、静電容量の経時的劣化が著しいか、または電極の単位体積当りの静電容量が不足で、新規用途開発の障害となっていた。

【解決手段】本発明においては水蒸気賦活されたヤシ殻活性炭であって、中位径が6～10μm、且つBET比表面積が1000～1500m²/gである活性炭を電解液を使用する電気二重層コンデンサの電極として用いることにより、電極の単位体積当り高い静電容量を長期に亙り保持する電気二重層コンデンサの開発に成功した。

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TAKEDA CHEM IND LTD

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(72)Inventor : ADACHI KIYOSHI
KUROSAKI TAKEO

(54) ACTIVE CARBON FOR ELECTRODE OF ELECTRIC DOUBLE-LAYER CAPACITOR

(57)Abstract:

PROBLEM TO BE SOLVED: To enable an electrode to be kept high in electrostatic capacitance per volume for a long term by a method wherein coconut shell steam-activated carbon prescribed in average diameter and BET specific surface is used as material for the electrode of an electric double-layer capacitor which employs electrolyte.

SOLUTION: Activated carbon used for the electrode of an electric double-layer capacitor which used electrolyte is formed of steam-activated coconut shell carbon 6 to 10 \times m in average diameter and 1000 to 1500m²/g in BET specific surface. Coconut shells are carbonized through a thermal treatment carried out under carbonizing conditions and ground into 10 to 100-mesh powder, and carbonized shell powder of mesh 10 to 100 is steam-activated at a temperature of 850°C or so for preferably 30 minted to 5 hours. The grain size of the activated carbon powder is 6 to 10 \times m in average diameter by measurement with a coal tar counter. It is preferable that the activated carbon powder is 1250 to 1450m²/g in BET specific surface when solvent used for a capacitor is propylene carbonate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to activated carbon suitable as an electrode of the electric double layer capacitor which uses the electrolytic solution.

[0002]

[Description of the Prior Art] It is a capacitor using the electric double layer produced in the interface of a solid-state and a liquid, electrostatic capacity of an electric double layer capacitor is very large compared with a cell, and excels also in a charge-and-discharge cycle property or boosting charge and is maintenance free, and since there is no possibility of causing environmental pollution, it attracts attention as a small backup power supply of a microcomputer or an IC memory especially recently. The above-mentioned solid-state in an electric double layer capacitor is a polarizable electrode, and powdered activated carbon is usually used. The electrolytic solution used for an electric double layer capacitor is divided roughly into an organic solvent system and a water-solution system. Since an organic solvent system has high withstand voltage, it is advantageous to a miniaturization, and it can also use a metal for sheathing. By the water-solution system, since the conductivity of the electrolytic solution is high, it is fit for low equivalent-series-resistance(ESR)-ization, and it is not influenced by humidity but has the description of excelling in environmental capability. In the electric double layer capacitor which has such an advantageous property, if the electrostatic capacity per unit volume of an electrode can be raised further, the application does not only remain in the backup power supply of a microcomputer or an IC memory, for example, is promising also as power sources, such as a pre-heater of the initial drive of various motors, an electric vehicle, and an exhaust gas purification catalyst. Then, in order to obtain the electric double layer capacitor of the one-layer high capacity per unit volume of an electrode, various amelioration has so far been tried. One of them has amelioration of the activated carbon used as an electrode.

[0003] Since the capacity of a capacitor element is determined by the surface area of the activated carbon electrode to be used, and the electric double layer capacity in the electrolytic solution, it is advantageous to use activated carbon with a big theory top specific surface area for aiming at improvement in a capacity consistency. then -- for example, petroleum coke was used as the raw material as shown in JP,63-78514,A, and bulk density called [specific surface area] it 0.2-1.0g [ml] /, total pore volume 0.5 - 3.0 ml/g by 2000-3500m²/g -- use to the electrode of high specific-surface-area activated carbon is proposed comparatively. Moreover, what has the property by the activated carbon with which the oxygen atom / carbon atomic ratio of activated carbon have the property or more of 0.1 especially phenol resin system activated carbon, and activated carbon using phenol resin as a binder is proposed as an electrode of a high capacity electric double layer capacitor by JP,7-135127,A. Furthermore, the carbonaceous material of high electrostatic capacity which heat-treats an activated carbon raw material at less than 700 degrees C during the hydroxide bath of alkali metal, and is obtained is also proposed in special playback Taira 03-812203.

[0004]

[Problem(s) to be Solved by the Invention] However, although there are some which

show very high electrostatic capacity called more than the 250 (farads F) / ml immediately after manufacture, the so-called chemical activation charcoal by which activation was carried out with chemicals, such as alkali and a zinc chloride, among the activated carbon for electric double layer capacitor electrodes proposed until now. If the electrostatic capacity causes a remarkable fall with the passage of time and passes six months or more in a short time, the electrostatic capacity will fall or less [of the time of manufacture] to 1/10, and it will be hard to present practical use with it. On the other hand, although there is almost no fall of electrostatic capacity with the passage of time, the activated carbon manufactured with the activation method by chemicals, such as steam activation. By the thing using an organic solvent system electrolyte, among what has so far been put in practical use, at most 20 F/g the thing using about eight F [ml] /and a water-solution system electrolyte -- at most -- it is 40 F/g and about 16 F/ml, and it is necessary to raise the electrostatic capacity per the electrode volume much more further for the new application development mentioned above

[0005]

[Means for Solving the Problem] Electrostatic capacity more this invention persons size per unit volume in order to obtain the becoming electric double layer capacitor electrode. The result of having repeated research wholeheartedly about mutual relation, such as a class of raw material of the powdered activated carbon to be used, an activation method, specific surface area of activated carbon, and particle diameter, By the BET specific surface area of 1000-1500m²/g a little lower than the thing of the BET specific surface area of 2000-3500m²/g which is activated carbon by which steam activation was carried out, and was considered to be suitable to obtain electrostatic capacity high until now. The electric double layer capacitor of high electrostatic capacity is given. and the particle size of the activated carbon with which the median diameter has 6-10 micrometers and so far been used in this field -- a little -- size -- the activated carbon which has particle size -- unexpected -- per unit volume of an electrode -- ***** -- And the high electrostatic capacity continued at the long period of time for six months or more, carried out the knowledge of saying [hardly falling], and completed this invention. Namely, this invention is coconut husks activated carbon by which (1) steam activation was carried out. The activated carbon for electrodes of the electric double layer capacitor with which a median diameter uses 6-10 micrometers and the electrolytic solution whose BET specific surface area is 1000-1500m²/g, (2) A median diameter is activated carbon given in 7 - (1) which is 9 micrometers, and (3) electrolytic solutions are the things of an organic solvent system. Activated carbon (1) whose a BET specific surface area is 1200-1500m²/g, or given in (2), and (4) electrolytic solutions are the things of a water-solution system. the electric double layer capacitor electrode with which activated carbon (1) whose a BET specific surface area is 1000-1300m²/g, or given in (2), and (5) electrolytic solutions consist of activated carbon of (1), (2), or (4) publications which are a sulfuric acid, and activated carbon given in (6) and (1) -- it comes out.

[0006]

[Embodiment of the Invention] Coconut husks with few contents of impurities, such as sulfur, are used for the raw material of the activated carbon used for this invention. On the usual carbonization conditions, for example, 400-800 degrees C, it heat-treats for 30 minutes to about 3 hours, and carbonizes, and it crushes to 10-100 meshes, and these coconut husks are usually the temperature around about 850 degrees C, and carry out

steam activation of the 500-1000 degrees C of the obtained coconut shell charcoal over 30 minutes - 5 hours for 10 minutes to 10 hours preferably. In this steam activation, if activation temperature is low and activation time amount is short, therefore the specific surface area of the activated carbon obtained will serve as smallness and activation time amount will become [activation temperature] high for a long time, specific surface area serves as size. The obtained activation charcoal is rinsed and dried, it grinds to the target grain size, and a classification adjusts grain size as occasion demands. 6-10 micrometers of median diameters which measured the grain size of the activated carbon which suits the purpose of this invention with the Coulter counter are 7.5-8.5 micrometers still more preferably seven to 9 micrometer preferably. The solvent which the BET specific surface area of the activated carbon is the thing of 1000-1500m²/g, and is used especially for an electric double layer capacitor moreover, for example In the case of an organic solvent system like propylene carbonate, as a BET specific surface area of activated carbon, usually 1200-1500m²/g, Preferably [it is desirable and] to 1250-1450m²/g and a pan the case where it is 1300-1400m²/g and a solvent is a water-solution system like a sulfuric acid -- usually -- 1000-1300m²/g -- desirable -- 1050-1250m²/g -- it is 1100-1200m²/g still more preferably. Moreover, it is usually 0.500-0.650g/ml, when especially the electrolytic solution is an organic solvent system, its ml is desirable in 0.530-0.600g /, and when it is a water-solution system, ml is desirable [the apparent density by the tap method of activated carbon] in 0.570-0.640g /. for manufacturing the electrode of an electric double layer capacitor using the activated carbon of this invention -- the very thing -- a well-known approach is employable. For example, the mixture of activated carbon, a binder, and water is often kneaded with a mixer. The obtained paste-like mixture is rolled out using a roll, extension-under heating processing of about 200-300 degrees C is carried out, and it carries out to suitable thickness, for example, an about 0.6mm sheet-like electrode material. This sheet-like electrode material is pierced to disc-like, and it considers as a polarizable electrode.

[0007] Thus, the obtained disc-like object can be piled up through 2-several sheet separator, it can contain in a sheathing container, and an electric double layer capacitor unit cell can be made by pouring in the electrolytic solution into it. As the electrolytic solution, there are a thing of an organic solvent system and a thing of a water-solution system. both the various 4th class phosphonium salt with which propylene carbonate is common with the phosphonium salt and is known as an electrolyte as a solvent of the organic solvent system electrolytic solution until now, and quarternary ammonium salt -- although -- it can be used. As the water-solution system electrolytic solution, although a dilute sulfuric acid is common, other mineral salt (4 boric-acid [for example,] fluoride), a nitric acid, etc. can be used. The water solution which furthermore makes a solute the mineral salt of hydroxylation potash, a sodium hydroxide, ammonium hydroxide, etc. can also be used expedient. The concentration of each electrolyte can be suitably chosen in 10 - 90% of the weight of the range.

[0008] Example 1 coconut husks were carbonized at 400-800 degrees C for 1 hour, under 850-degree C heating, it washed and dried, rotary kiln ground what carried out steam activation for 180 minutes for 120 minutes for 90 minutes for 60 minutes, respectively, and powdered activated carbon (activated carbon 1-4) with a median diameter [by measurement of a Coulter counter] of 7 or 5 micrometers was obtained. The disc-like electrode with a diameter [of 15mm] and a thickness of 0.6mm was made from each

activated carbon, two of them were made to pile up mutually and the electrode of a capacitor unit cell was made. The physical properties of each obtained powdered activated carbon and the made above-mentioned electrode, and 4(C₂H₅) PBF₃ The electrostatic capacity immediately after manufacture of the electrostatic capacity immediately after manufacture of the capacitor unit cell made using 0.5 mols / propylene carbonate electrolytic solution and the unit cell six months after manufacture and the electrostatic capacity of the unit cell for manufacture six months are measured, and the result is shown in [Table 1].

[Table 1]

[0009] example 2 coconut husks -- 400-800 degrees C -- 1 hour -- carbonizing -- a fluidized bed furnace -- the bottom of 900-degree C heating -- steam activation was carried out for 180 minutes, it washed, and drying grinding was carried out and powdered activated carbon (activated carbon 5-8) with a median diameter of 7 or 5 micrometers was obtained for 120 minutes for 90 minutes for 60 minutes, respectively. The electrode of a capacitor unit cell was made from each activated carbon like the example 1. The electrostatic capacity of the capacitor unit cell six months immediately after the physical properties of each obtained powdered activated carbon and manufacture of the made above-mentioned electrode and the capacitor unit cell made using the sulfuric-acid electrolytic solution 40% and after manufacture is measured, and the result is shown in [Table 2].

[Table 2]

[0010] The activated carbon of 1350m²/[of BET specific surface areas] g made like example 3 example 1 was obtained, this was ground and six kinds of powdered activated carbon (activated carbon 9-14) with which particle size differs, respectively was obtained. The physical properties of activated carbon and the electrostatic capacity of a capacitor unit cell are measured by the same approach as an example 1, and the result is shown in [Table 3].

[Table 3]

TECHNICAL FIELD

[Field of the Invention] This invention relates to activated carbon suitable as an electrode of the electric double layer capacitor which uses the electrolytic solution.

[0011] The activated carbon of 1140m²/g of BET specific surface areas] g made like example 4 example 2 was obtained, this was ground and six kinds of powdered activated carbon (activated carbon 15-20) with which particle size differs, respectively was obtained. The physical properties of activated carbon and the electrostatic capacity of a capacitor unit cell are measured by the same approach as an example 2, and the result is shown in [Table 4].

[Table 4]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, although there are some which show very high electrostatic capacity called more than the 250 (farads F) / ml immediately after manufacture, the so-called chemical activation charcoal by which activation was carried out with chemicals, such as alkali and a zinc chloride, among the activated carbon for electric double layer capacitor electrodes proposed until now If the electrostatic capacity causes a remarkable fall with the passage of time and passes six months or more in a short time, the electrostatic capacity will fall or less [of the time of manufacture] to 1/10, and it will be hard to present practical use with it. On the other hand, although there is almost no fall of electrostatic capacity with the passage of time, the activated carbon manufactured with the activationsmethode by chemicals, such as steam activation By the thing using an organic solvent system electrolyte, among what has so far been put in practical use, at most 20 F/g the thing using about eight F [ml] /and a water-solution system electrolyte -- at most -- it is 40 F/g and about 16 F/ml, and it is necessary to raise the electrostatic capacity per the electrode volume much more further for the new application development mentioned above

[0012]

[Effect of the Invention] The reservation of high electrostatic capacity by which gave the electrode of high electrostatic capacity per unit volume of an electrode, and degradation by the repeat and the passage of time of charge and discharge was moreover continued and stabilized low at the long period of time is possible for the activated carbon for electrodes of the electric double layer capacitor of this invention

CLAIMS

[Claim(s)]

[Claim 1] Activated carbon for electrodes of the electric double layer capacitor with which it is coconut husks activated carbon by which steam activation was carried out, and a median diameter uses 6-10 micrometers and the electrolytic solution whose BET specific surface area is 1000-1500m²/g.

[Claim 2] Activated carbon according to claim 1 whose median diameter is 7-9 micrometers.

[Claim 3] Activated carbon according to claim 1 or 2 whose electrolytic solution is the thing of an organic solvent system and whose BET specific surface area is 1200-1500m²/g.

[Claim 4] Activated carbon according to claim 1 or 2 whose electrolytic solution is the thing of a water-solution system and whose BET specific surface area is 1000-1300m²/g.

[Claim 5] Activated carbon according to claim 1, 2, or 4 whose electrolytic solution is a sulfuric acid.

[Claim 6] The electric double layer capacitor electrode which consists of activated carbon according to claim 1.